

## Supporting Information

Electroactive metal-organic framework-based novel on-off  
ratiometric electrochemical platform for effective detection of  
lead ions

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## **1. Additional Experimental Section.**

### **1.1 Reagents and Materials**

Zirconium chloride ( $\text{ZrCl}_4$ ,  $\geq 99.9\%$ ) was purchased from Aladdin Industrial Corporation (Shanghai, China). 2,2'-bipyridine-5,5'-dicarboxylic acid ( $> 98\%$ ) and acetic acid ( $\geq 99.5\%$ ) were purchased from Shanghai Titan technology Co., Ltd., (Shanghai, China) and Tianjin Beichen Founder Reagent Factory (Tianjin, China), respectively.  $\text{Pb}(\text{NO}_3)_2$  ( $\geq 99\%$ ) was obtained from Tianjin Beilian Fine Chemicals Development Co., Ltd., (Tianjin, China). N,N-Dimethylformamide and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Graphene oxide (GO) was purchased from Nanjing XFNano Material Technology Co., Ltd., (Nanjing, China). The aqueous solutions were prepared with ultrapure water ( $\geq 18 \text{ M}\Omega\cdot\text{cm}$ ) from a Millipore system.

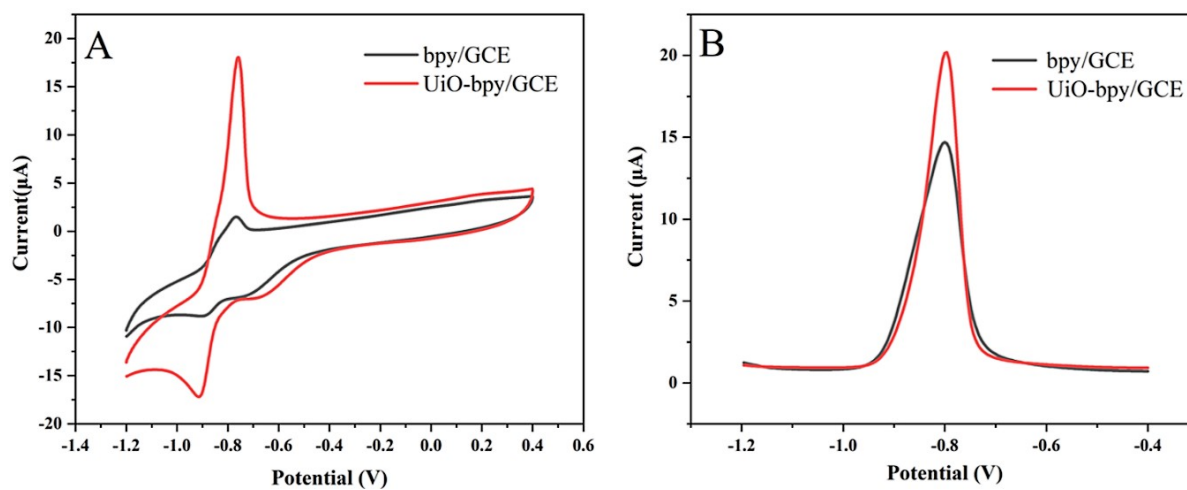
### **1.2 Instrumentations**

CHI 840D electrochemical analyzer (Shanghai CH Instruments, China) with a three-electrode system (glassy carbon working electrode, saturated calomel reference electrode and Pt plate auxiliary electrode) was used for electrochemical tests. X-ray diffraction (XRD, Rigaku D-MAX 2500/PC, Japan), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB XI+, USA), Fourier transform infrared spectroscopy (FT-IR, Nicolet 510P, USA), scanning electron microscopy (SEM, JSM-7500F, Japan), and raman spectra (inVia, Renishaw, UK) technologies were adopted for material characterization.

### **1.3 Electrochemical test**

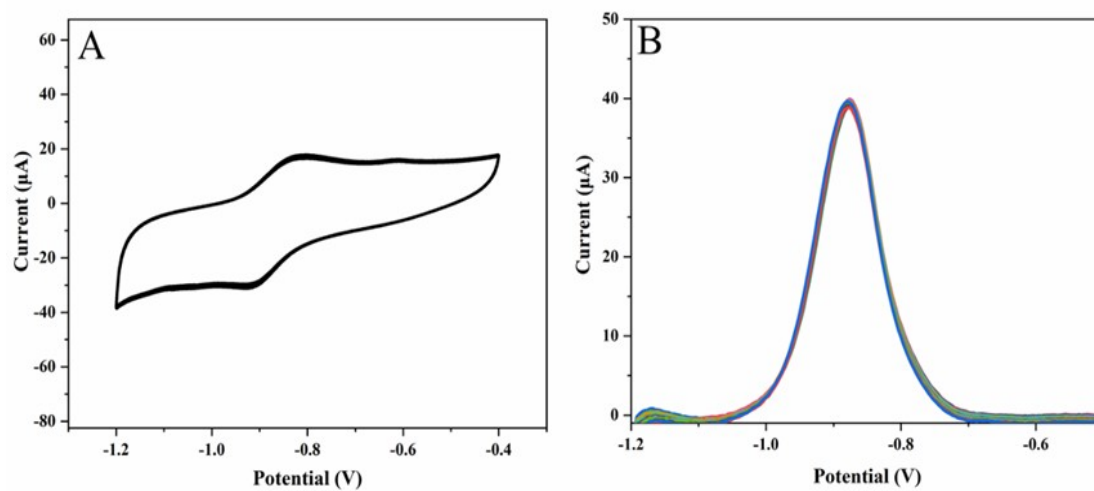
The electrochemical behavior of the modified electrode was characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in 0.1 M KCl containing 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  and 1.0 mM  $[\text{Fe}(\text{CN})_6]^{4-}$  ( $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ). The potential range of CV test was -0.2 V ~ 0.6 V, and the scan rate was 0.1 V/s. The experimental conditions for the EIS test were as follows: amplitude = 0.005 V, applied potential = 0.2 V, voltage frequency range from 100 kHz to 0.01 Hz. Differential pulse anodic stripping voltammetry (DPASV) was adopted for  $\text{Pb}^{2+}$  detection. The detection electrolyte solution is 0.1 M ABS. The experimental conditions were as follows: amplitude = 0.05 V, pulse width = 0.05 s, pulse period = 0.2 s. Unless otherwise indicated, the deposition potential and deposition time were -1.2 V and 100 s, respectively.

## 2. Electrochemical behaviors of the bpy/GCE and UiO-bpy/GCE.



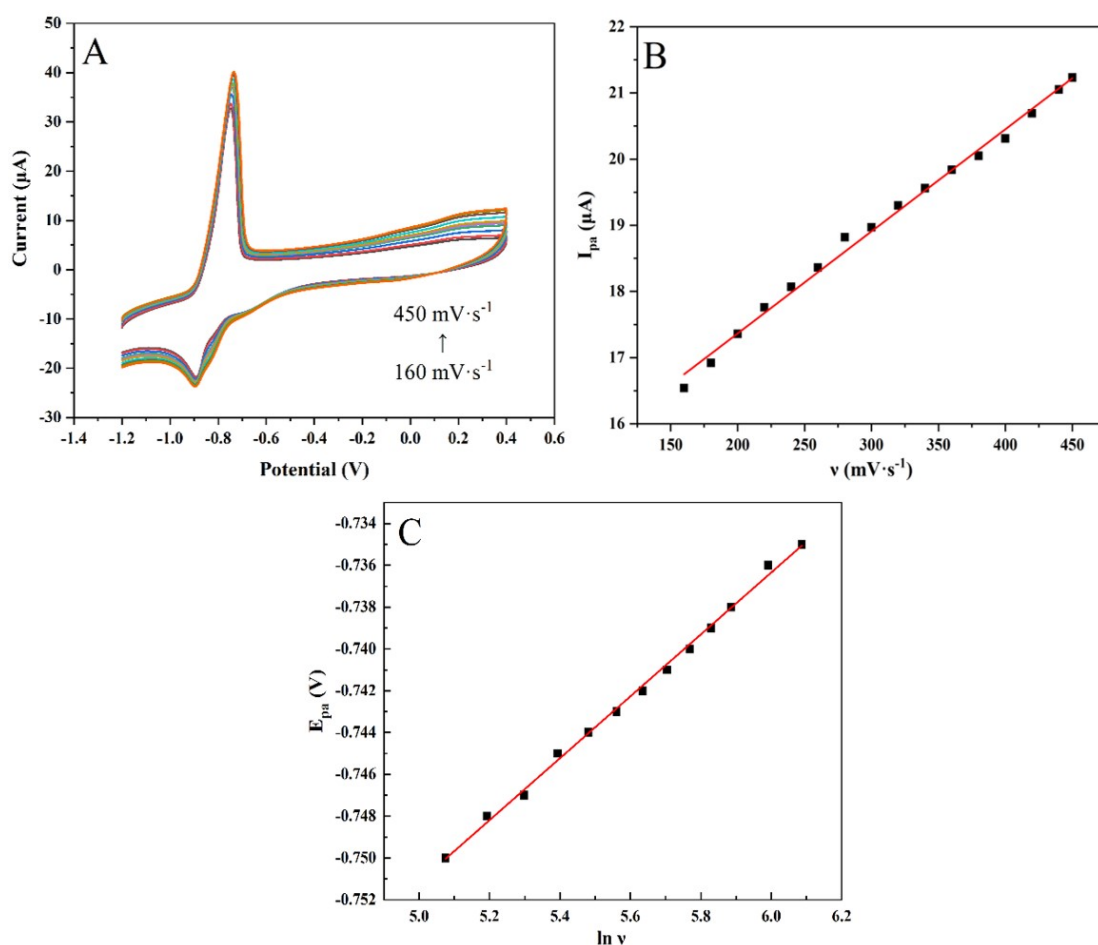
**Fig. S1.** (A) CV and (B) DPASV curves of the bpy/GCE and UiO-bpy/GCE in 0.1 M ABS (pH 5).

### 3. Electrochemical signal stability tests of the rGO/UiO-bpy/GCE.



**Fig. S2.** (A) CV curves for consecutive ten cycles and (B) DPASV curves for fifteen measurements on the rGO/UiO-bpy/GCE in 0.1 M ABS (pH 5).

#### 4. Effect of scan rate on oxidation peak current and oxidation peak potential.



**Fig.S3.** (A) CV plots of the UiO-bpy/GCE in 0.1 M ABS (pH 5) under different scan rates (from 160 to 450 mV·s<sup>-1</sup>). (B) The linear graph of I<sub>pa</sub> vs v. (C) The linear graph of E<sub>pa</sub> vs ln v.

Fig. S3A shows the CV plots of the UiO-bpy/GCE in 0.1 M ABS (pH 5) under different scan rates (v), and the effect of v on oxidation peak current (I<sub>pa</sub>) and oxidation peak potential (E<sub>pa</sub>) are displayed in Fig. S3B and C. As is shown in Fig. S3B, the I<sub>pa</sub> of the UiO-bpy/GCE increases linearly with v in a range of 160 to 450 mV·s<sup>-1</sup>, and the linear equation can be depicted as:

$$I_{pa} (\mu A) = 0.01542 v (\text{mV} \cdot \text{s}^{-1}) + 14.28 (R^2=0.995) \quad (1)$$

This indicates that the electrochemical process on UiO-bpy/GCE surface follows the adsorption control mechanism as expected<sup>1</sup>. In addition, the E<sub>pa</sub> moves positively

with the increase of  $v$ , the linear relationship between  $E_{pa}$  and  $\ln v$  is expressed as:

$$E_{pa} \text{ (V)} = 0.0148 \ln v \text{ (mV}\cdot\text{s}^{-1}) - 0.8251 \text{ (R}^2=0.997) \quad (2)$$

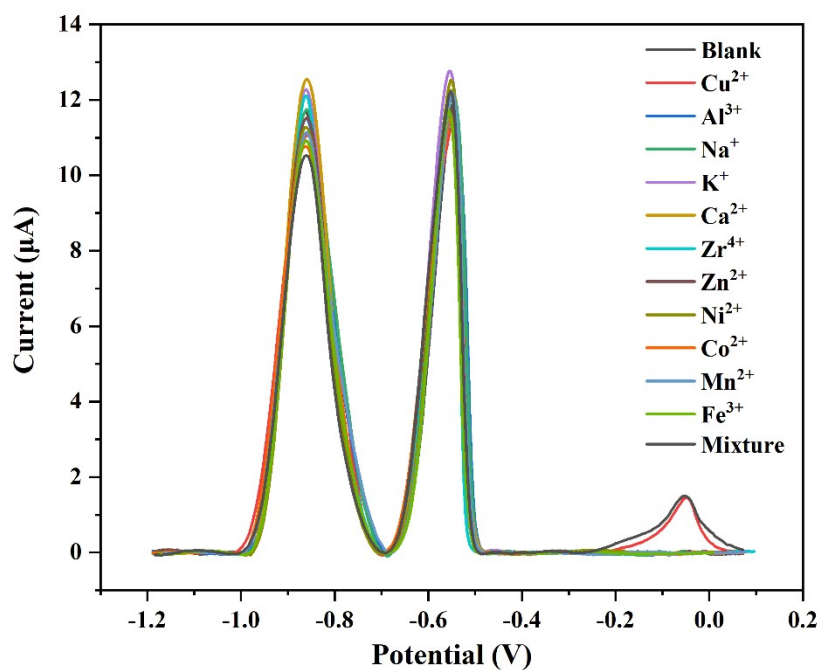
According to the Laviron equation <sup>2</sup>:

$$E_{pa} = E_0 + \frac{RT}{\alpha n \alpha F} \ln \left( \frac{RTk^0}{\alpha n F} \right) + \frac{RT}{\alpha n F} \ln v \quad (3)$$

Where  $E_0$  represents the formal standard potential,  $k^0$  represents the rate constant,  $R$ ,  $T$  and  $F$  stand for their general physical meanings,  $\alpha$  represents the transfer coefficient, and  $n$  is the number of transferred electrons in the reaction. According to Eqs. (2) and (3), the value of  $\alpha n$  can be calculated as 1.735. Usually, the value of  $\alpha$  ranges from 0.3 to 0.7 <sup>3</sup>, so the value of  $n$  may be 3 or 4.



## 5. The voltammograms in the interference study.



**Fig. S4.** DPASV curves of the rGO/UiO-bpy/GCE in 0.1 M ABS (pH 6) containing 0.5  $\mu\text{M}$   $\text{Pb}^{2+}$  and different interfere ions with concentration of 2.5  $\mu\text{M}$ .

## References

1. P. Zhao, L. Huang, H. Wang, C. Wang, J. Chen, P. Yang, M. Ni, C. Chen, C. Li, Y. Xie and J. Fei, *Sens. Actuators B Chem.*, 2022, **350**, 130853.
2. T. Xue, Y. Sheng, J. Xu, Y. Li, X. Lu, Y. Zhu, X. Duan and Y. Wen, *Biosens. Bioelectron.*, 2019, **145**, 111716.
3. Y. Zhang, G. I. N. Waterhouse, Z. P. Xiang, J. Che, C. Chen and W. Sun, *Food Chem.*, 2020, **326**, 126976.